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REPORT

MRL-R-1024

CORRELATION OF ABEL HEAT TEST TIME AND STABILIZER CONTENT OF AGED GUN PROPELLANTS

M.A. Parry, D.J. Pinson and E. Wanat

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A study of old MRL records was undertaken to assess the extent of correlation between the two traditional prime "stability indicators" of gun propellants; the Abel Heat test time and the stabilizer concentration. The analysis reveals that the Abel Heat test does not have as universal an application as has been generally accepted in the past. The use of the heat test as a method for screening propellants for possible deterioration has limitations for double base propellants and has severe limitations for triple base propellants.

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Correlation of abel heat test time and stabilizer content of aged gun propellants

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ABSTRACT

A study of old MRL records was undertaken to assess the extent of correlation between the two traditional prime stability indicators of gun propellants; the Abel Heat test time and the stabilizer concentration. The analysis reveals that the Abel Heat test does not have as universal an application as has been generally accepted in the past. The use of the heat test as a method for screening propellants for possible deterioration has limitations for double base propellants and has severe limitations for triple base propellants.

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CORRELATION OF ABEL HEAT TEST TIME AND STABILIZER CONTENT OF AGED GUN PROPELLANTS

1. INTRODUCTION

It is well established that gun propellants must be adequately stabilized to guard against spontaneous ignition of the propellant during extended storage. At production, the level of stabilizer is checked and stability tests are conducted on each lot of propellant. As a secondary safeguard, the Inspection Services request DSTO to conduct accelerated ageing tests of each lot of freshly produced propellant, to ensure that the propellant will not deteriorate rapidly during Service use or during bulk storage. Furthermore, the *Inspection Services* conduct a surveillance programme on propellants. Samples are periodically withdrawn from storage and subjected to a number of tests, including stability tests.

These tests were conducted by Explosives Testing Group (ETG) at Materials Research Laboratories (MRL) from 1944 until the late 1970s when the responsibility was transferred to Nitrocellulose Propellants Group at Weapons Systems Research Laboratories (WSRL) in South Australia. While MRL are no longer active or expert in the propellant field, it was felt that a summary of past MRL results might yield a useful contribution to the problem of propellant stability. This work became more relevant when, in 1983, a large quantity of propellant in a magazine spontaneously ignited in one of our (then) Department of Defence Support Factories. This type of incident has occurred many times in overseas storage depots and highlights the need for a rigorous surveillance programme.

The periodical inspection of bulk stocks of propellant for the Australian Army is regulated by the document AQAS OP 118/1 (PROV) [1]. This schedule describes inspection procedures for stored propellant and lists test levels to indicate the suitability of the propellant for continued safe storage and use. Three methods are used to assess the stabilizer content; the Abel heat test, colour number and the analysis of stabilizer concentration. In general, but not always, the preliminary step in the assessment of chemical stability during surveillance testing is an Abel heat

test, followed by chemical analysis of stabilizer if the heat test result is low. The effectiveness of the surveillance procedure is therefore extremely dependent upon the Abel heat test providing an effective "screen" for deteriorated propellants.

In this report, we have assessed the extent of correlation of heat test time and concentration of effective stabilizer for twenty gun propellants subjected to accelerated ageing at MRL. It was anticipated that these two "stability indicators" would show adequate correlation and would confirm the philosophy of current surveillance procedures and the use of the Abel heat test.

Most of the propellants discussed are older formulations and contained diphenylamine (DPA) or ethyl centralite (EC) as stabilizers. Although a range of modern methods are now available for the analysis of these stabilizers and their degradation products which form on ageing, the concentrations of stabilizer cited in this study were obtained with older analytical methods [2,3]. These methods yielded a result referred to as "effective stabilizer", since only the unreacted stabilizer and early degradation products of the stabilizer are analysed and these are known to be efficient stabilizers. The analytical methods were reproducible and accurate and are not considered to be a significant source of error in this study.

The Abel heat test is one of the oldest propellant stability tests. It was first introduced by Sir Frederick Abel in 1866 as a test for the stability of gun cotton [4]. The test involves heating a small sample of propellant at an elevated temperature and measuring the time for the development of a reference tint on a special indicator paper which is sensitive to nitrogen dioxide. The heat test time is taken as a comparative measure of the stability of the propellant; short times indicate that the stored bulk propellant contains less stabilizer and is approaching a dangerous condition with the possible risk of spontaneous ignition. There have been considerable differences of opinion on the precise significance of the test since its introduction, although the conditions are now more carefully controlled and standardized [5]. It was assumed that factors known to affect the test, such as; method of preparation of the sample, light intensity of the test room, operator dependency, impurities, moisture content and condition of the indicator paper would provide a background error in our analysis.

2. SUMMARY OF MRL TRIALS AND EVALUATION

To conduct the accelerated ageing trials at MRL approximately 2.25 kg of propellant was placed in a glass tube of dimensions 63.5 mm ID and 840 mm long (for sticks) and 57.2 mm ID and 686 mm long (for powders). The tubes were corked at both ends and placed in chambers maintained at 49°C. Samples were tested initially and then at intervals of 12 months to determine the extent of chemical degradation. Such tests were continued for periods of 2 to 5 years depending on the type of propellant and were referred to as "climatic trials 49°C tube tests (dry)".

Table 1 lists the propellants investigated and shows the dates over which samples were on trial at MRL. All of the single base propellants were DPA stabilized whereas all of the double and triple base propellants were stabilized with EC. DPA and EC concentrations were determined by an analytical method which included separation by steam distillation, followed by bromination. Analysis was then completed gravimetrically [2,3].

The Abel heat test was conducted according to published procedure [5]. The heat test temperature was chosen according to the type of propellant on trial. In general, freshly produced, single base propellants, were tested at 82°C and after accelerated ageing they were tested at 71°C. In general, double and triple base propellants were tested at 65.5°C, both before and after ageing.

Colour tests and pH determinations were also carried out for double and triple base propellants although the results are not discussed in this report.

3. TYPICAL RESULT FOR A PROPELLANT

In Table 2 we have reproduced the information obtained from an old accelerated ageing trial of a lot of propellant NH025. This propellant formulation contains a nominal 1% of DPA stabilizer and analysis confirmed this level as 0.90% in lot MEM 109. The Abel heat test was conducted at 82°C and a result of greater than 30 minutes was obtained. It was a generally accepted practice to terminate the test after 30 minutes if the reference tint had not fully developed on the indicator paper. We see that further ageing at 49°C for 5 years produced a decline in both stabilizer concentration and Abel heat test time.

4. SENTENCING PROCEDURE FOR PROPELLANTS

Reference [1] describes the inspection procedures, test conditions and sentencing procedures for gun propellants in bulk storage. The sentencing schedule for propellant NH (and similar propellants) is reproduced in Table 3. If the heat test time is greater than 10 minutes then the propellant lot is retested after 3 years, for between 6 and 10 minutes the lot is retested after 2 years, and if between 4 and 6 minutes the propellant is analysed for stabilizer. When the effective DPA is greater than 0.5% then the lot is retested after 1.5 years whereas less than 0.5% DPA requires the lot to be rejected. When the heat test time falls below 4 minutes the lot is destroyed, regardless of other tests.

Similar sentencing procedures are detailed in Reference [1] for double and triple base propellants.

5. RESULTS AND DISCUSSION

To assess if any relationship existed between "effective stabilizer" content and Abel heat test time, scatter diagrams of the two parameters were plotted (Figures 1 to 10) for propellants with similar compositions and a common sentencing schedule as summarized in Table 3. The composition of each propellant is indicated on each figure and abbreviations used for various components are listed in Table 4.

Figure 1 shows results for many lots of the propellant NH025 after ageing. For heat tests which were terminated at 30 minutes, the data points are stacked and so results above the dotted line are not absolute values but are plotted only for an indication of frequency. Analysis of the data in Figure 1 yields a correlation coefficient of 0.8 between these two qualitative parameters for propellant NH025, assuming a simple linear correlation. Certainly a general trend exists where decreasing stabilizer gives an decreasing heat test time.

Figure 2 shows the results obtained for AR4001, another single base propellant stabilized with DPA. Unlike Figure 1 this plot contains the results obtained at different heat test temperatures; 82^{o}C on freshly produced propellant and 71^{o}C on aged propellant. These results for AR4001 give a correlation coefficient of 0.9. However, the plot also indicates that about six lots of this propellant had degraded more rapidly than other lots, showing heat test times lower than 5 minutes and less than 0.1% of stabilizer. Three of these lots had reached this stage after only 3 years of accelerated ageing.

Figures 3 to 10 are diagrams produced for propellants NH049, NH055, FNH/P, FNH016, FNH025, IMR4831, IMR4879 and AR2201. Figure 3 is in colour to better illustrate the spread of results for NH049. All these propellants show a trend of decreased heat test time with low residual stabilizer but correlations vary from poor to fairly good. Propellants IMR4879 and AR2201 (Figures 9 and 10) both show poor stabilizer-heat test time correlations (0.5 and 0.65). Of particular concern are the high heat test readings obtained for lots of aged propellant where the effective stabilizer is very low. For example, in Figure 10 a heat test reading of 27 minutes was obtained for a lot of the propellant AR2201 aged for 5 years where the stabilizer content had degraded to about 0.05%. From Figure 8 we find that propellant IMR4831 maintains high heat test times at stabilizer concentrations as low as 0.2%. Existing surveillance procedures for all the preceding 10 propellants mentioned require chemical analysis on these propellants only if the heat test time is less than 6 minutes. This could possibly lead to an inaccurate indication of the condition of the propellant. Furthermore, if the intention of the heat test limit of 6 minutes is to screen propellant lots with about 0.5% of effective DPA, then the screening test fails, though if higher heat test limits were selected, a useful screen could be provided for most of these propellants.

Figures 11 to 13 show the extent of correlation for three double base propellants stabilized with EC, namely M9, WT144-048 and CD/T. Of these three propellants M9 has the best correlation (0.83) while the other two are

poor. M9, with 0.75% EC has the shortest "life"; some lots of this propellant degrade to little stabilizer and low heat test times after only one year on trial. By comparison, all lots of the propellant CD/T (with 0.5% of EC), after 5 years of ageing, show heat test times greater than 10 minutes and contain more than 0.1% of residual EC.

Results for triple base propellants (Figures 14 to 20) indicate no statistical relationship between stabilizer content and heat test time. The correlation coefficients were all very low. All these propellants contain high concentrations of EC. Figure 20 is reproduced in colour to better identify the results after each year of accelerated ageing.

To investigate why there was such a difference between single and triple base propellants, mean heat test times and stabilizer levels were determined for each year of the accelerated ageing trial. Figures 21 and 22 show the deterioration rate profiles which are characteristic of all the DPA-stabilized single base propellants studied. The heat test times have large standard deviations in comparison with those of stabilizer content. Decreasing mean heat test times and mean stabilizer contents are observed on ageing. Figures 23 to 25 are characteristic of all the triple base propellants and the double base propellant CD/T. With an increasing period of accelerated ageing the effective stabilizer content drops, as expected, but the mean heat test time remains fairly constant or increases. This trend was confirmed after examining original data sheets for the individual lots of triple base propellants where it was often found that heat test times would increase after ageing of the propellant. Figure 20 confirms and highlights this effect for the propellant MNF/S. Figures 21 to 25 indicate that stabilizer levels reduce almost linearly with propellant ageing. The Abel heat test results reduce for all of the aged single base propellants.

This explains the poor and sometimes negative correlations of these two stability indicators for double and triple base propellants and also suggests that the heat test is inadequate for samples of aged double and triple base propellants of the type investigated.

Initially, it was proposed that EC was affecting the heat test, since all of the double and triple base propellants studied contain EC, but M9 exhibits a much better correlation than triple base propellants and it also contains EC. A more likely explanation to account for this phenomenon is the interference of nitroguanidine (NQ) with the heat test result. NQ is known to react with nitrogen dioxide [6] and we know that the indicator paper used in the Abel heat test is sensitive mainly to nitrogen dioxide evolution [7]. Furthermore NQ and EC form a crystalline complex [8] which may vary the reactivity of these materials during accelerated ageing and/or the subsequent Abel heat test.

6. CONCLUSIONS

The Abel heat test provides an indication of effective stabilizer content for most of the DPA-stabilized single base propellants studied,

although the results are somewhat scattered. However, it has a significant weakness as a screening test in that a high result (long heat test time) can be recorded for some propellants which contain very low effective stabilizer after accelerated ageing. The Abel Heat Test times specified in current procedures for sentencing aged gun propellants appear inadequate.

The double base propellant, M9, demonstrates a reasonable correlation between ethyl centralite (EC) and heat test time but the propellants CD/T and WT144-048 have a poor correlation even though there is a general trend between heat test time and effective stabilizer.

The results of seven triple base propellants reveal very poor correlations between heat test time and effective stabilizer. The variable results are possibly due to interference from NQ in the formulations or an NQ-EC complex.

If these trends persist for propellants stored under normal Service conditions and the current sentencing criteria are applied, then it is possible for a hazardous situation to arise. It is recommended that the correlation of Abel heat test results and stabilizer content be checked for normally-aged propellants.

There appears to be no value in applying the Abel heat test to samples of aged double and triple base propellants and the test should be replaced by appropriate methods of chemical analysis which will accurately estimate the residual stabilizer component.

7. ACKNOWLEDGEMENTS

The authors would like to express their appreciation to members of the Explosives Testing Group of MRL who planned and conducted the accelerated ageing trials from which the Abel Heat Test results were obtained, to Mr R.G. Davidson who performed the chemical analysis of stabilizer and to Mr R.P. Parker who assisted in the preparation of the diagrams.

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TABLE 1

PROPELLANTS INVESTIGATED

Single Base DPA Stabilized

(MRL Trials)

AR4401	(1966-1978)
AR2201	(1958-1968)
FNH/P	(1957-1979)
FNH025	(1957-1978)
FNH016	(1962-1978)
NH025	(1945-1957)
NH049	(1954-1960)
NH055	(1945-1970)
IMR4831	(1946-1951)
IMR4879	(1946-1965)

Double Base EC Stabilized

M9	(1966-1977)
CD/T	(1950-1960)
WT144-048	(1942-1948)

Triple Base EC Stabilized

NFQ042	(1944-1953)
NFQ/S	(1944-1954)
MNQF/SO32	(1969-1977)
NQ/S	(1946-1955)
NQ034	(1954-1979)
MNF2P/S 168-048	(1960-1978)
MNF/S	(1950-1968)

TABLE 2

AN EXAMPLE OF THE RESULTS OBTAINED FROM AN
ACCELERATED AGEING TRIAL AT 49°C
FOR A LOT OF PROPELLANT NH025

Identification No: GAM 1344
Lot No: MEM 109
Date Commenced: 10/1953

YEARS ON TRIAL	HEAT TEST (MINS)		STABILIZER "DPA"
	71°C	PAPER	
Initial	(82°C) 30+	1939J	0.90
1	30+	1946B	0.77
2	30+	1948A	0.63
3	22	1948C	0.54
4	9	1950A	0.41
5	8	1950C	0.35

TABLE 3

SENTENCING SCHEDULE FOR AR, NH, FNH,
IMR PROPELLANTS (REF. [1])

HEAT TEST AT 71.1°C (MINUTES)	DPA CONTENT % FOUND	SENTENCE RETEST AFTER
> 10	-	3 Years
6-10	-	2 Years
4-6	> 0.5	1-1/2 Years
	< 0.5	Reject
< 4		Destroy

TABLE 4

ABBREVIATIONS USED FOR COMPONENTS OF PROPELLANT FORMULATIONS

NC	nitrocellulose
NG	nitroglycerine
NQ	nitroguanidine (picrite)
EC	ethylcentralite (carbamite)
K	potassium nitrate or potassium sulphate
CR	cryolite
DNT	dinitrotoluene
DPA	diphenylamine
DBP	dibutylphthalate
DOP	dioctylphthalate
GR	graphite
MIN. JELLY	mineral jelly
T	tin

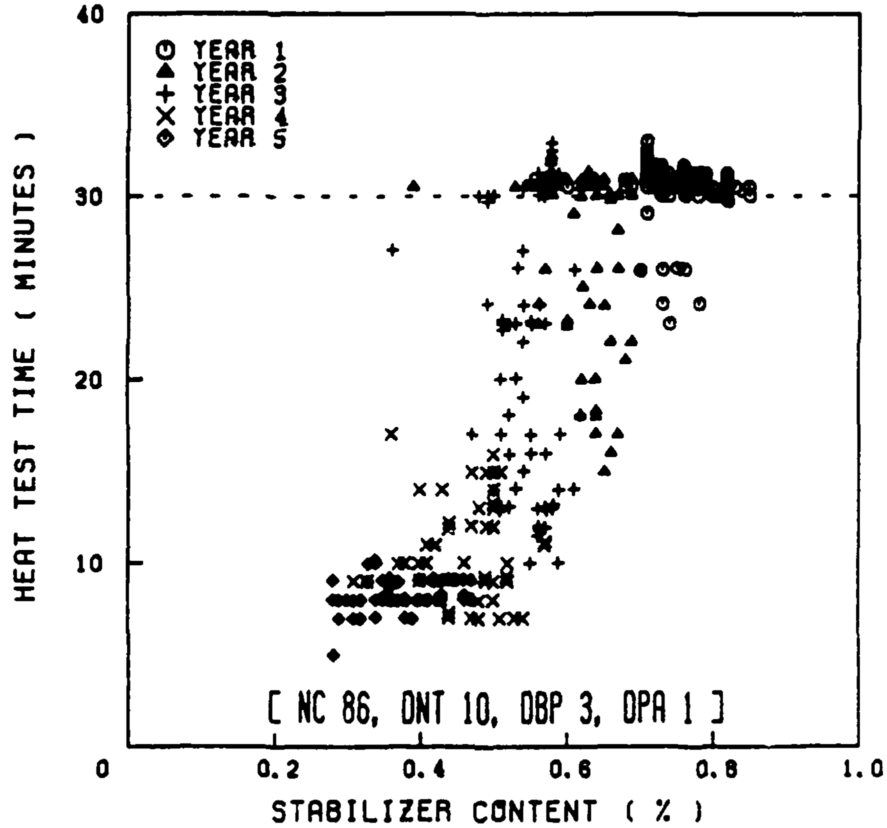

FIGURE 1 % Stabilizer (DPA) vs. heat test time, NH025 accelerated ageing 5 years, heat test temperature 71°C.

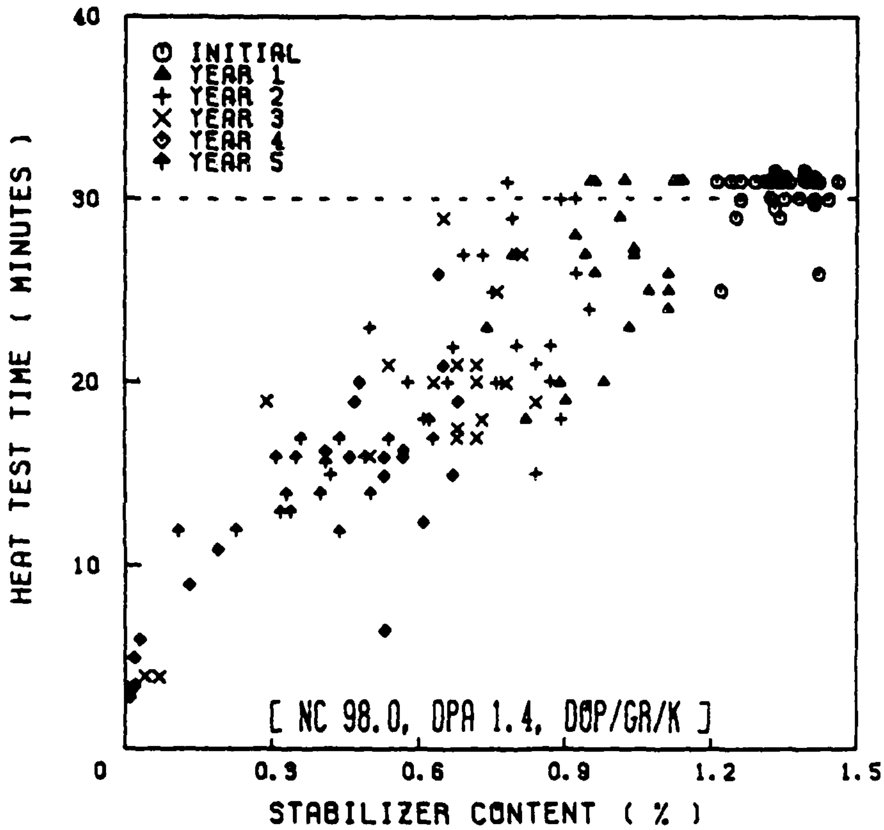

FIGURE 2 % Stabilizer (DPA) vs. heat test time, AR4001 accelerated ageing 5 years, heat test temperature 82°C initial, then 71°C.

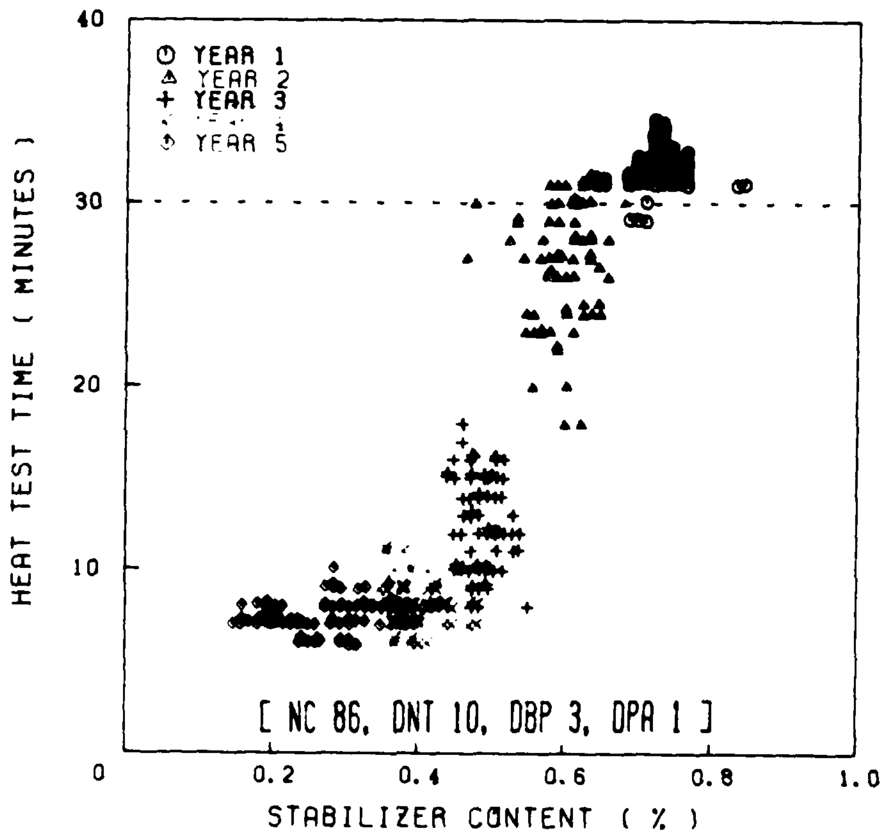

FIGURE 3 % Stabilizer (DPA) vs. heat test time, NH049 accelerated ageing 5 years, heat test temperature 71°C.

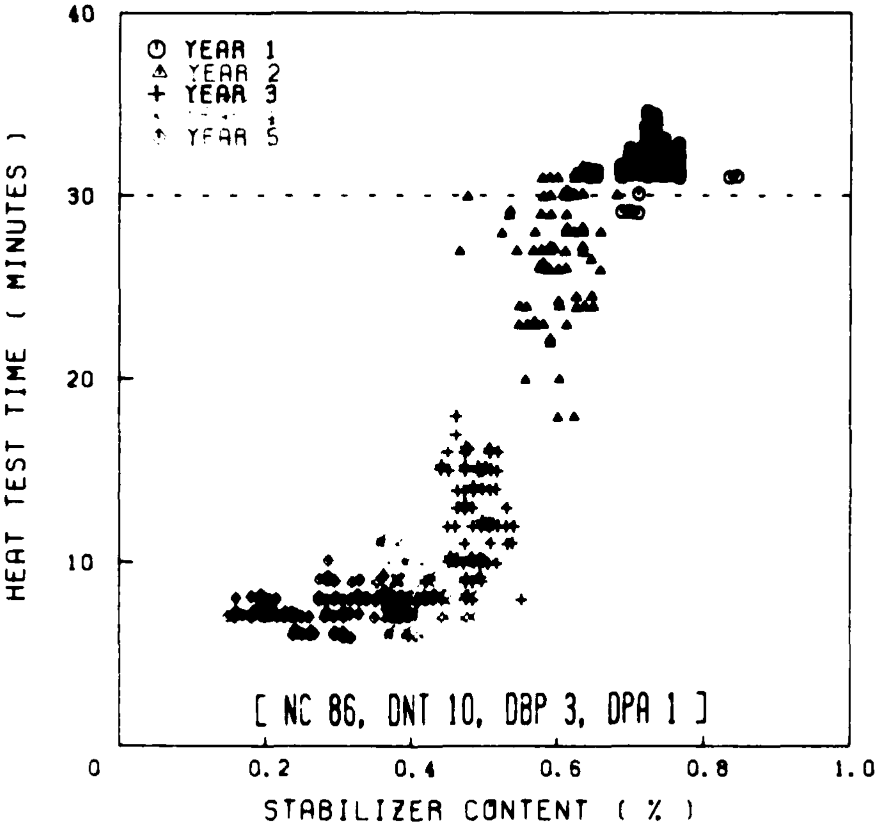

FIGURE 3 % Stabilizer (DPA) vs. heat test time, NH049 accelerated ageing 5 years, heat test temperature 71°C.

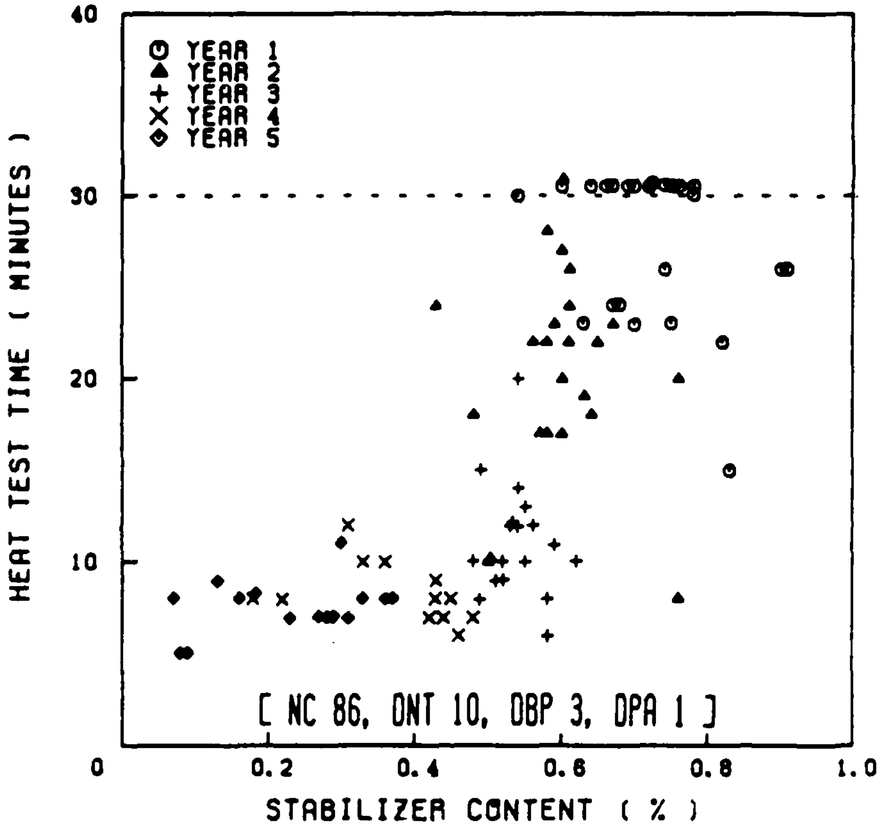

FIGURE 4 % Stabilizer (DPA) vs. heat test time, NH055 accelerated ageing 5 years, heat test temperature 71°C.

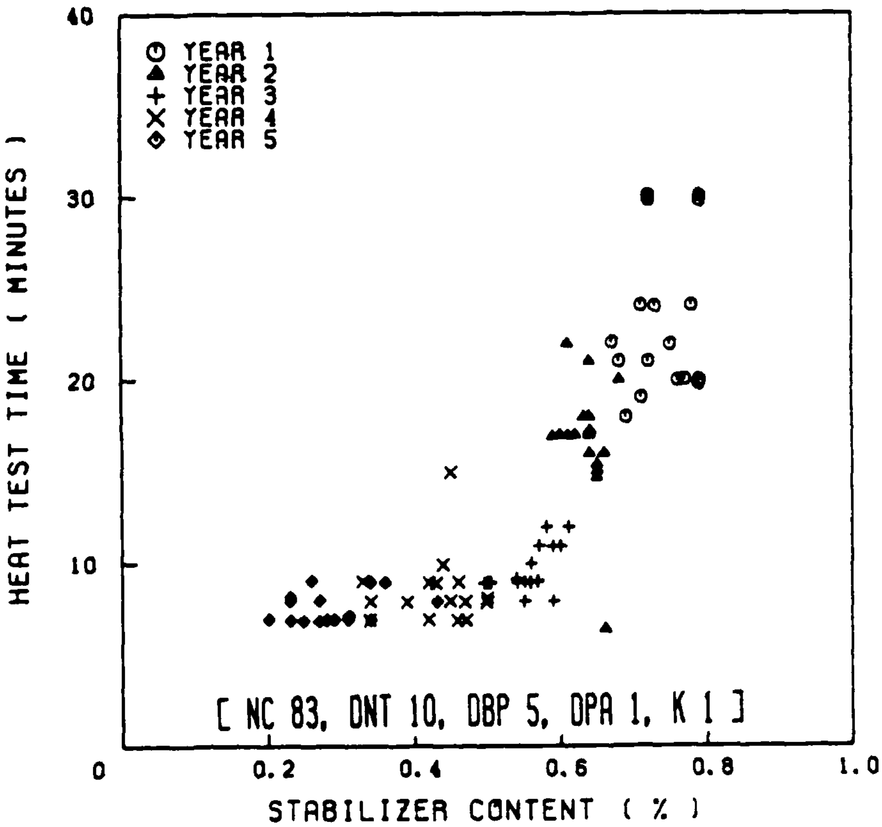

FIGURE 5 % Stabilizer (DPA) vs. heat test time, FNH/P accelerated ageing 5 years, heat test temperature 71°C.

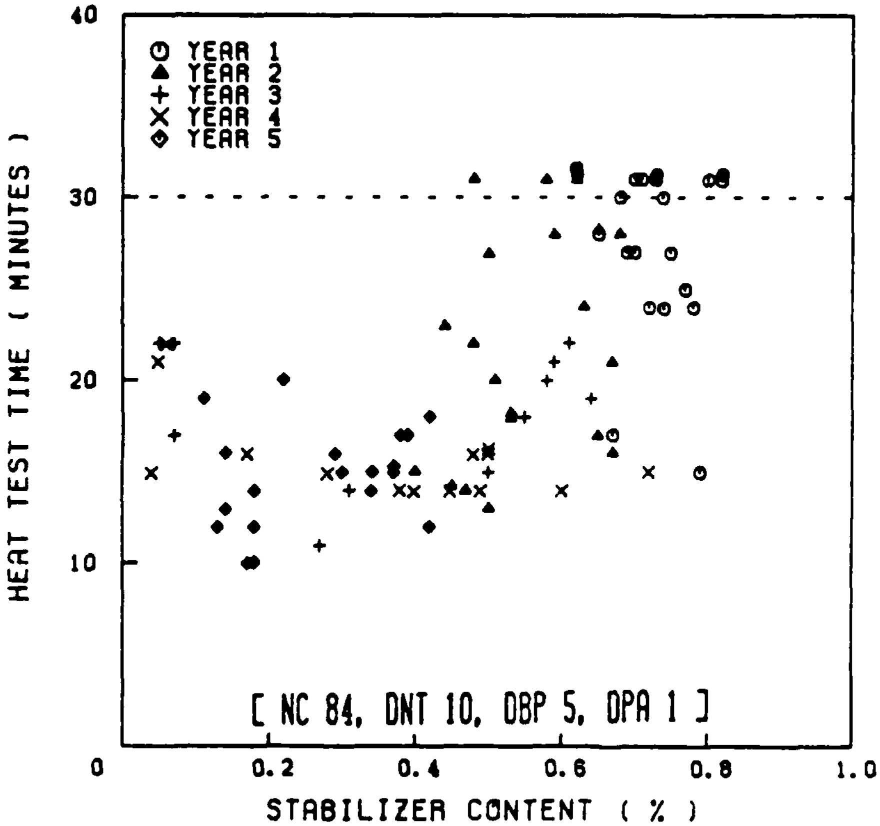

FIGURE 6 % Stabilizer (DPA) vs. heat test time, FNH016 accelerated ageing 5 years, heat test temperature 71°C.

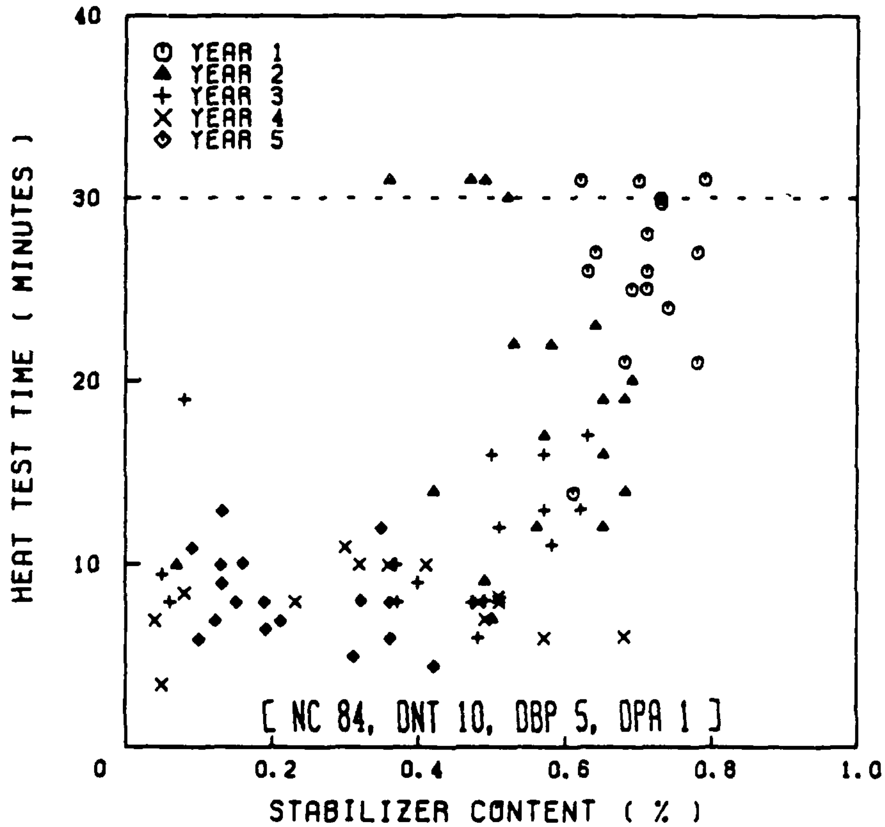

FIGURE 7 % Stabilizer (DPA) vs. heat test time, FNH025 accelerated ageing 5 years, heat test temperature 71°C.

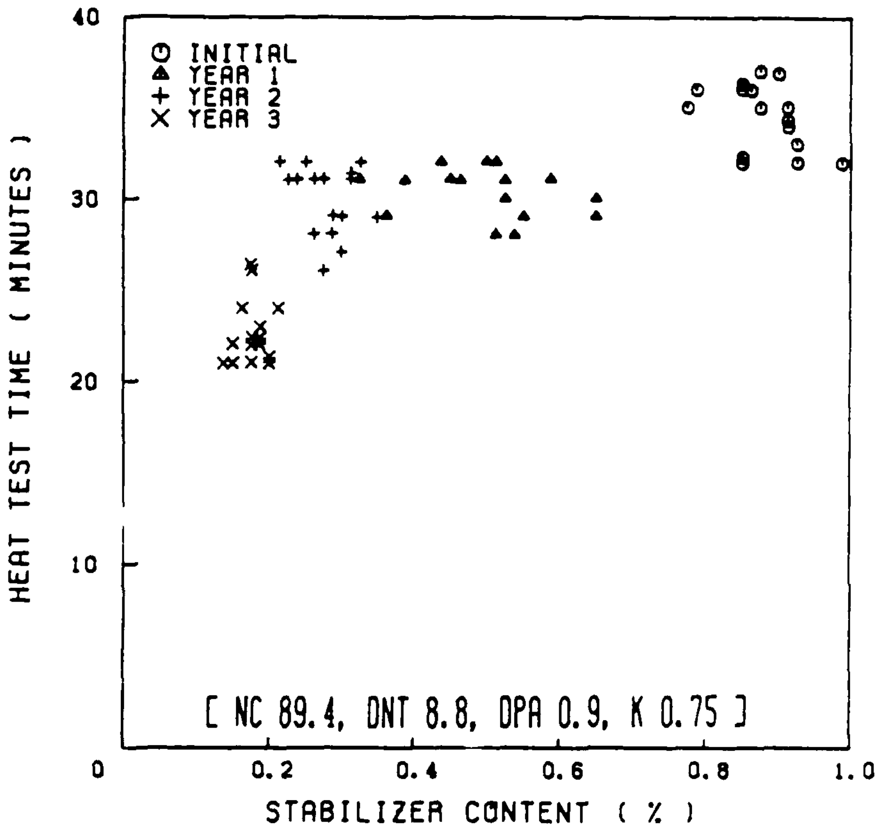

FIGURE 8 % Stabilizer (DPA) vs. heat test time, IMR4831 accelerated ageing 3 years, heat test temperature 71°C.

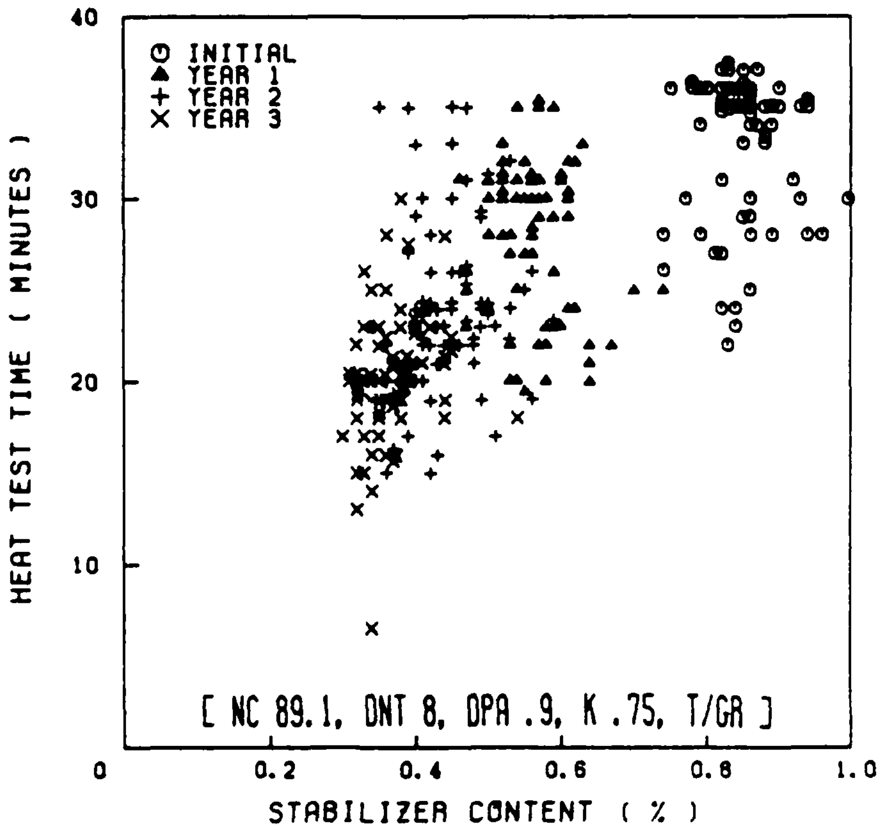

FIGURE 9 % Stabilizer (DPA) vs. heat test time, IMR4879 accelerated ageing 3 years, heat test temperature 71°C.

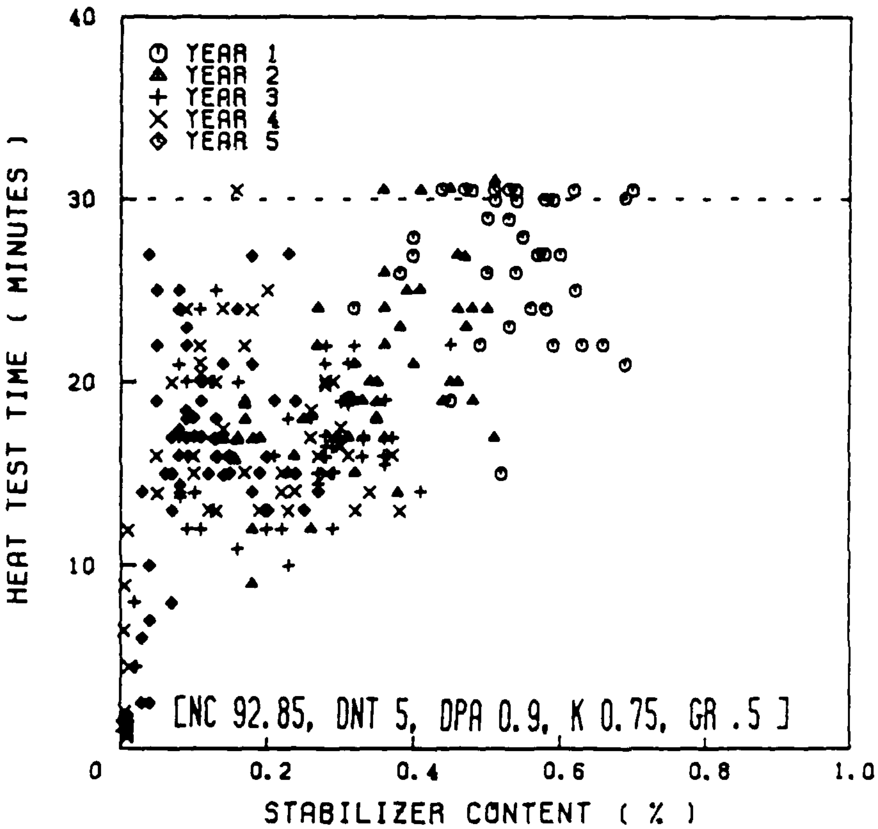

FIGURE 10 % Stabilizer (DPA) vs. heat test time, AR2201 accelerated ageing 5 years, heat test temperature 71°C.

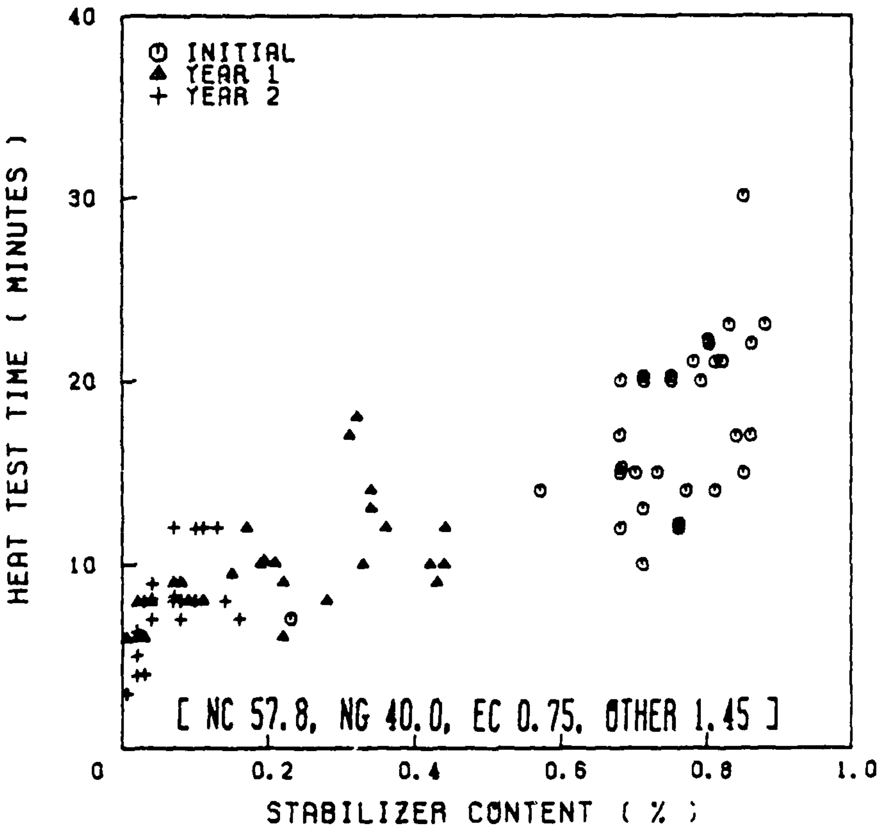

FIGURE 11 % Stabilizer (EC) vs. heat test time, M9 accelerated ageing 2 years, heat test temperature 71°C.

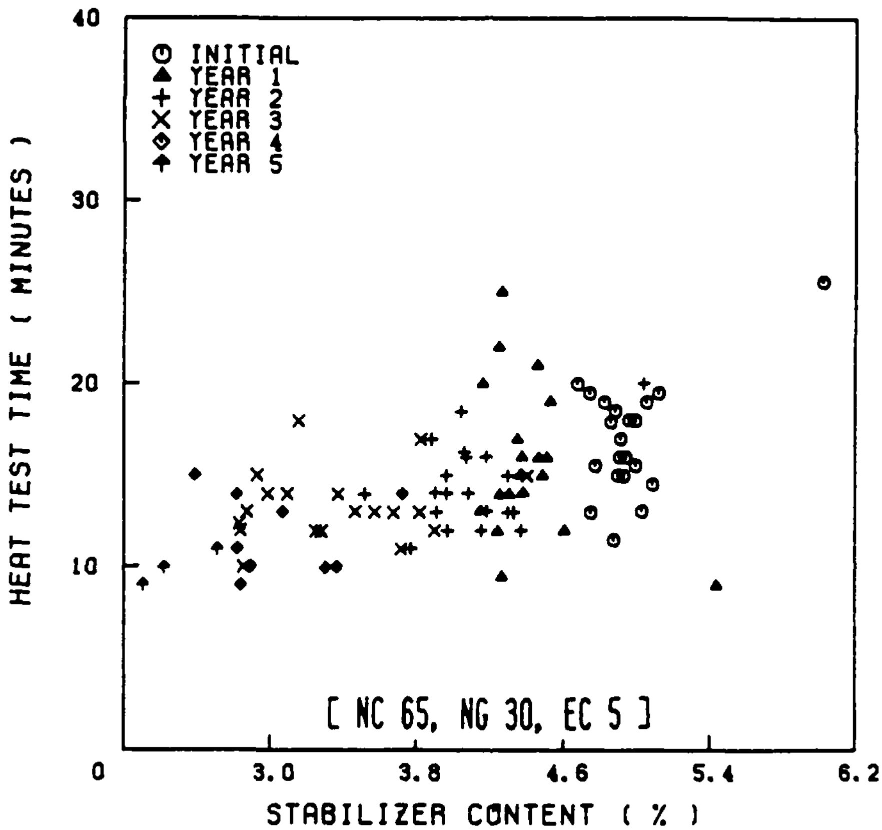

FIGURE 12 % Stabilizer (EC) vs. heat test time, WT144-048 accelerated ageing 5 years, heat test temperature 71°C initial, then 65.6°C.

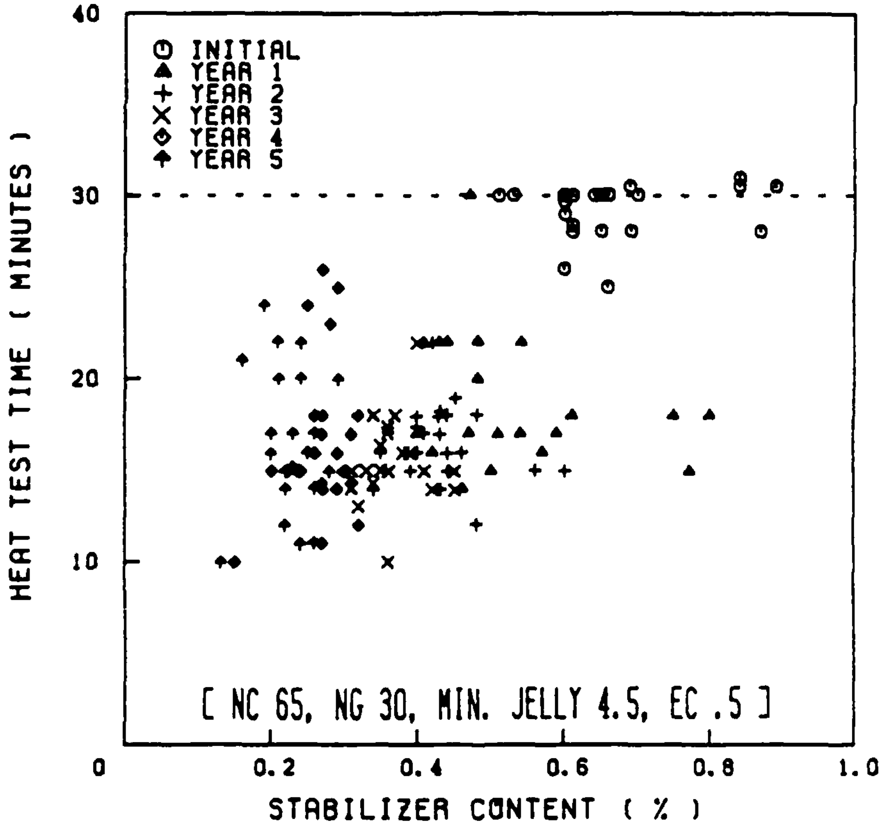

FIGURE 13 % Stabilizer (EC) vs. heat test time, CD/T accelerated ageing 5 years, heat test temperature 71°C.

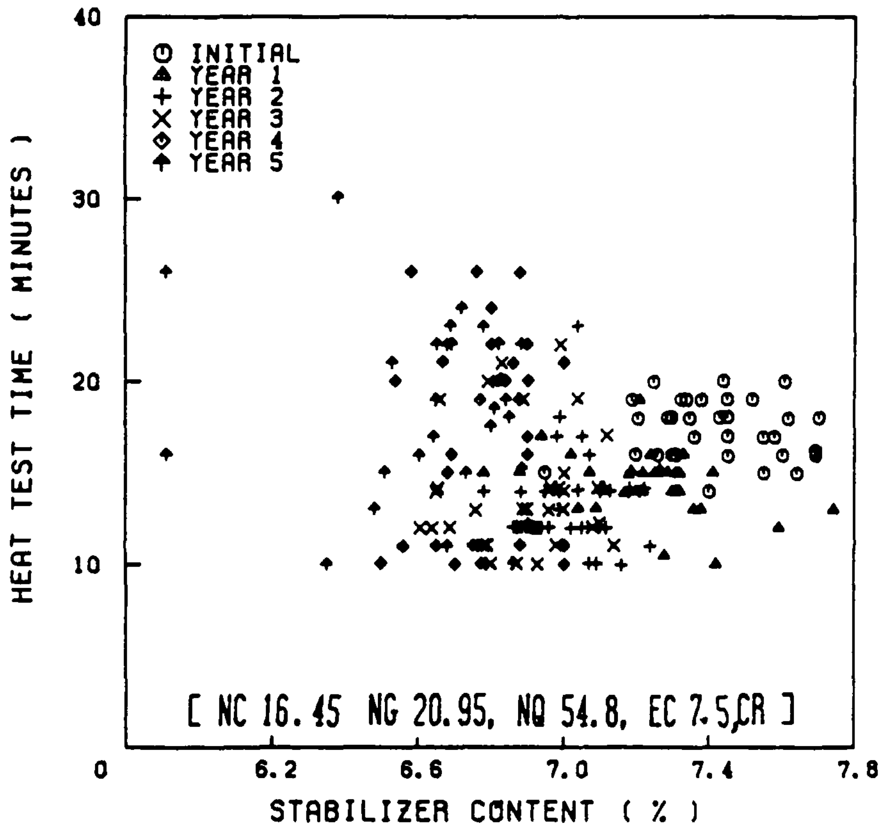

FIGURE 14 % Stabilizer (EC) vs. heat test time, NFQ042 accelerated ageing 5 years, heat test temperature 65.6°C.

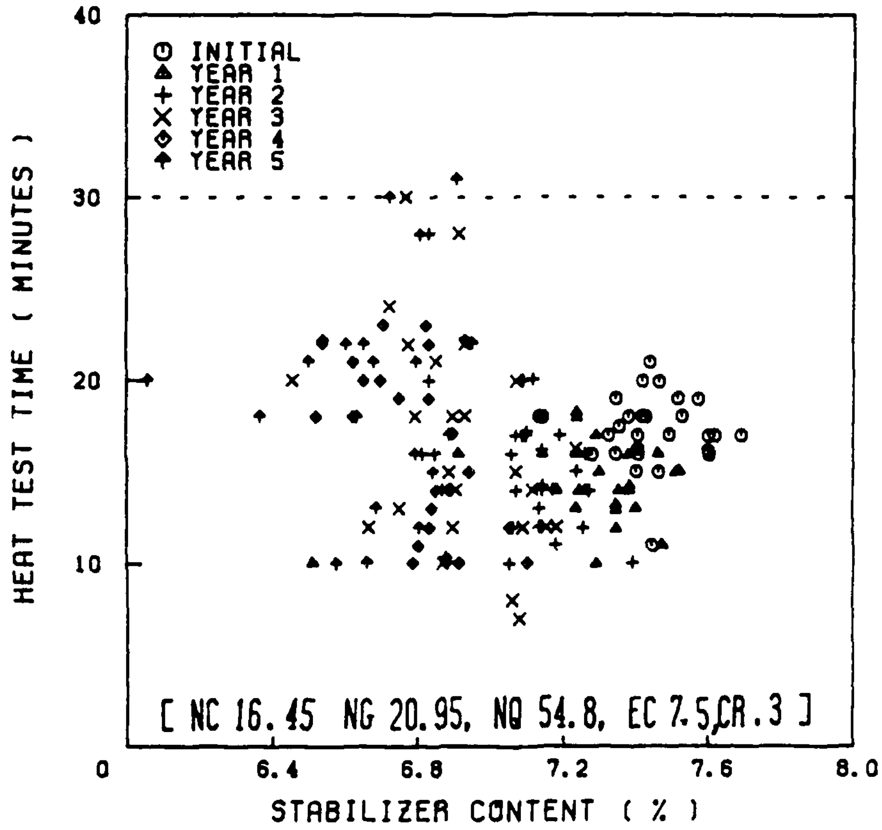

FIGURE 15 % Stabilizer (EC) vs. heat test time, NFQ/S accelerated ageing 5 years, heat test temperature 65.6°C.

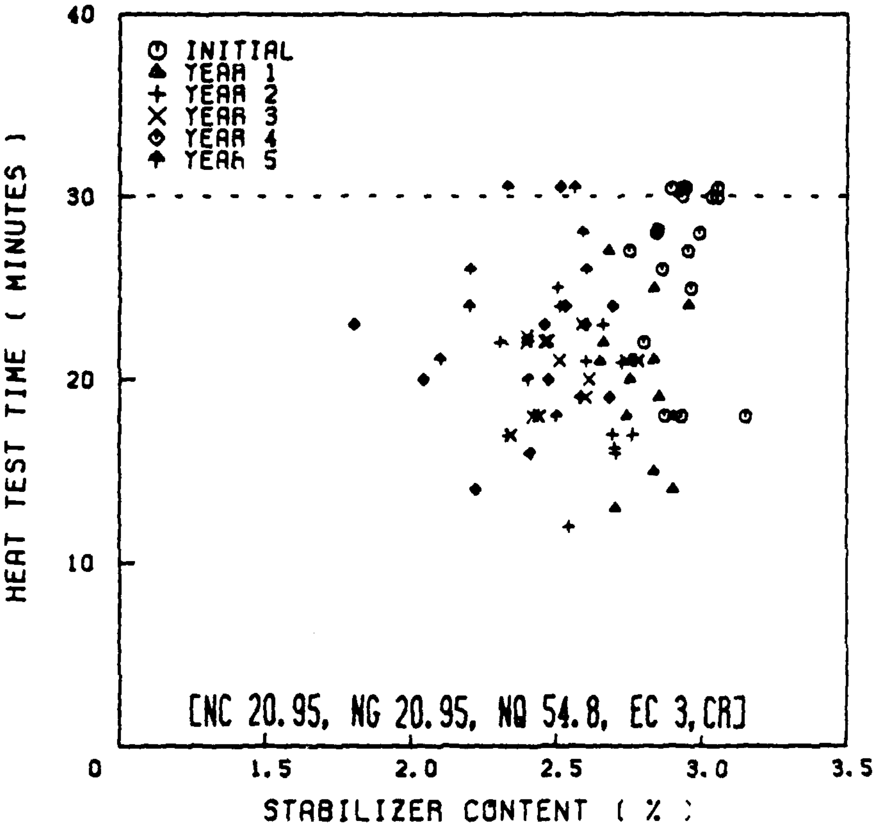

FIGURE 16 % Stabilizer (EC) vs. heat test time, MNFQ/S.032 accelerated ageing 5 years, heat test temperature 65.6°C.

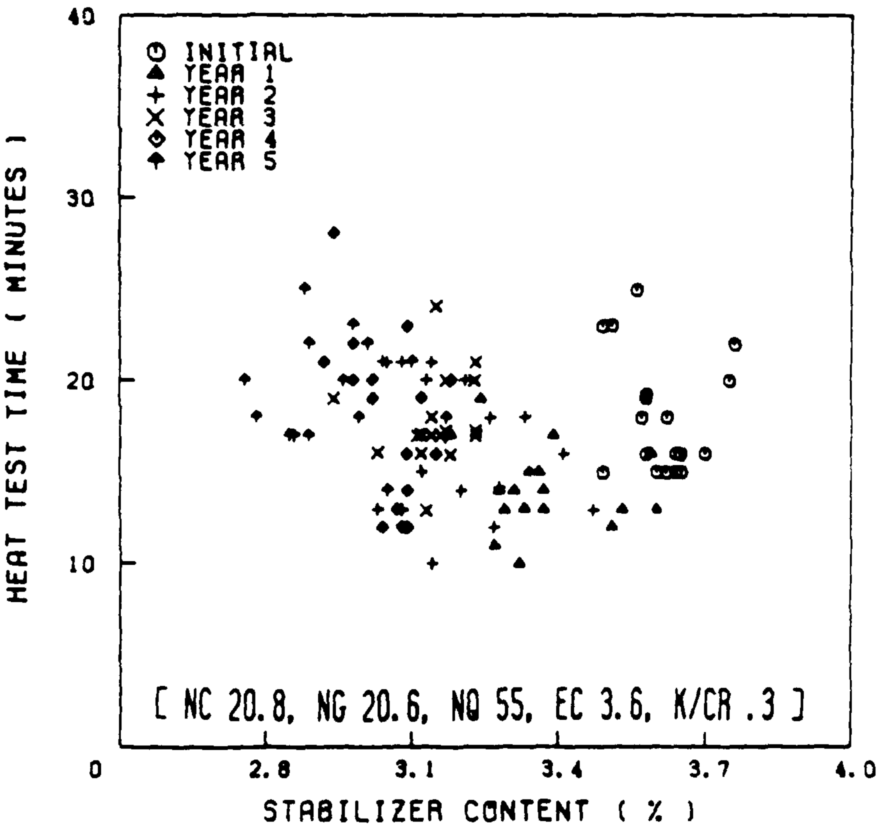

FIGURE 17 % Stabilizer (EC) vs. heat test time, NQ/S accelerated ageing 5 years, heat test temperature 65.6°C.

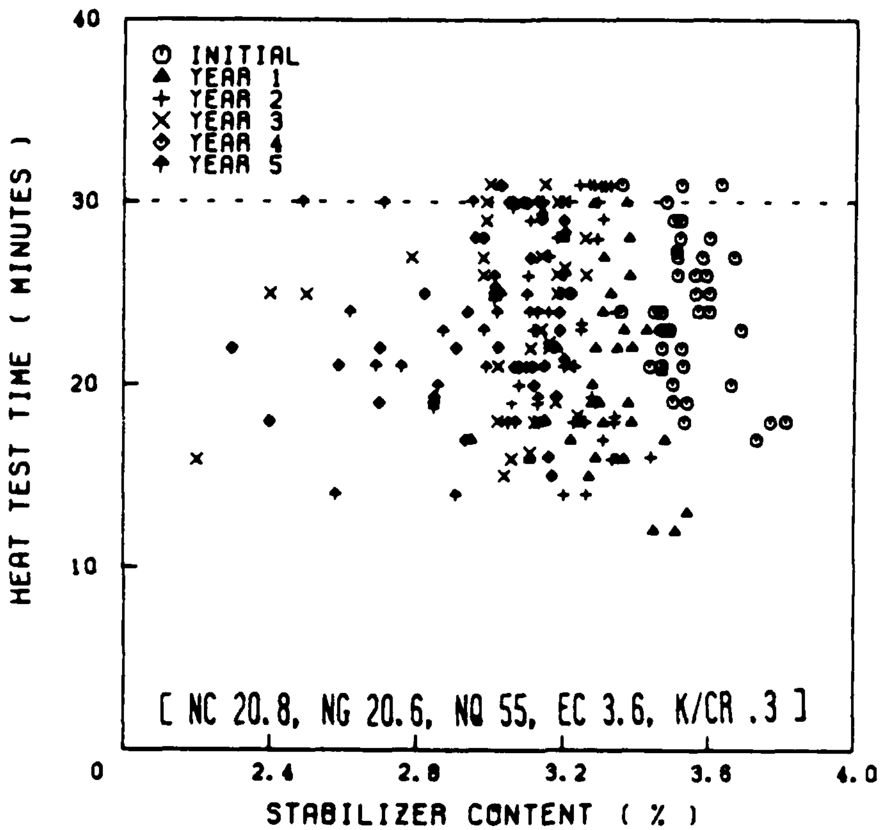

FIGURE 18 % Stabilizer (EC) vs. heat test time, NQ034 accelerated ageing 5 years, heat test temperature 65.6°C.

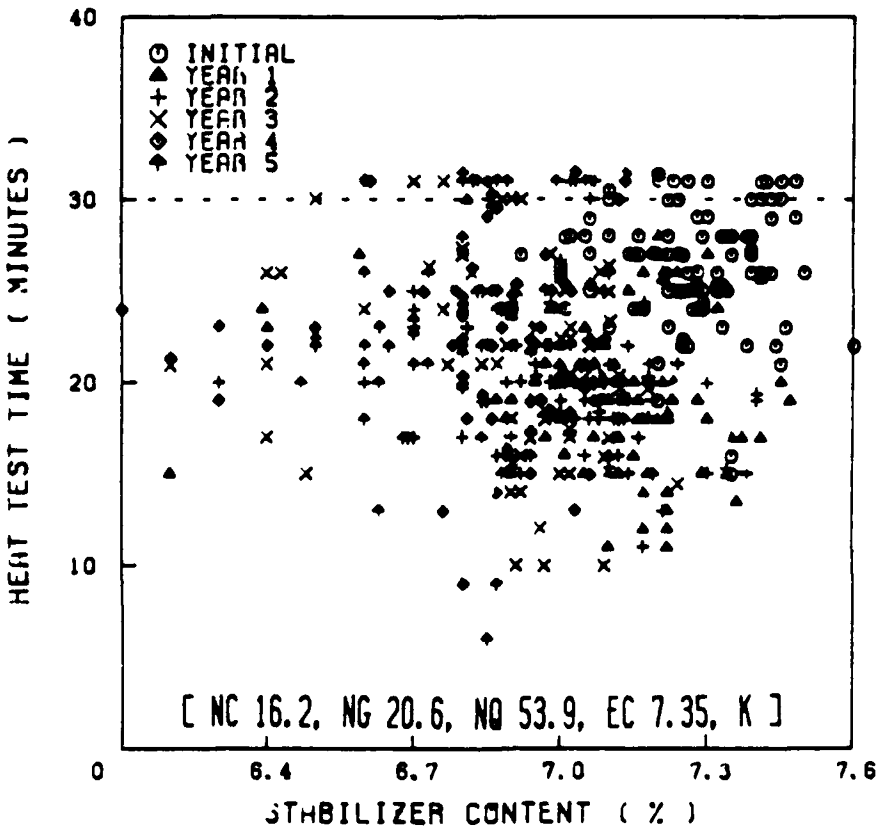

FIGURE 19 % Stabilizer (EC) vs. heat test time, MNF2P/S 168-048 accelerated ageing 5 years, heat test temperature 65.6°C.

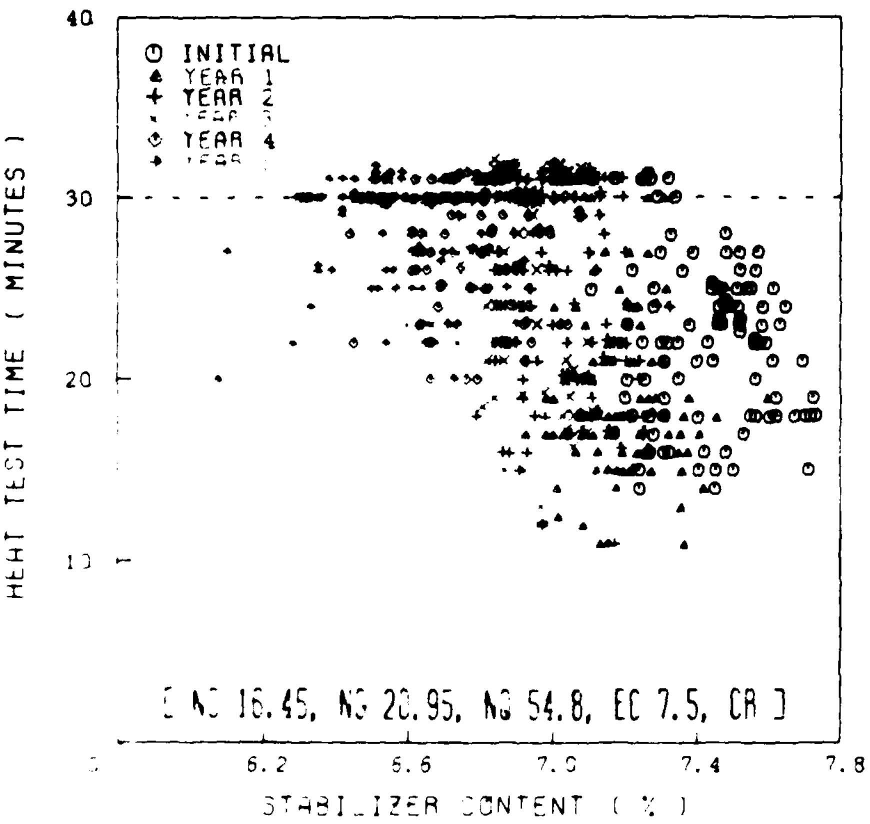

FIGURE 20 % Stabilizer (EC) vs. heat test time, MNF/S accelerated ageing 5 years, heat test temperature 65.6°C.

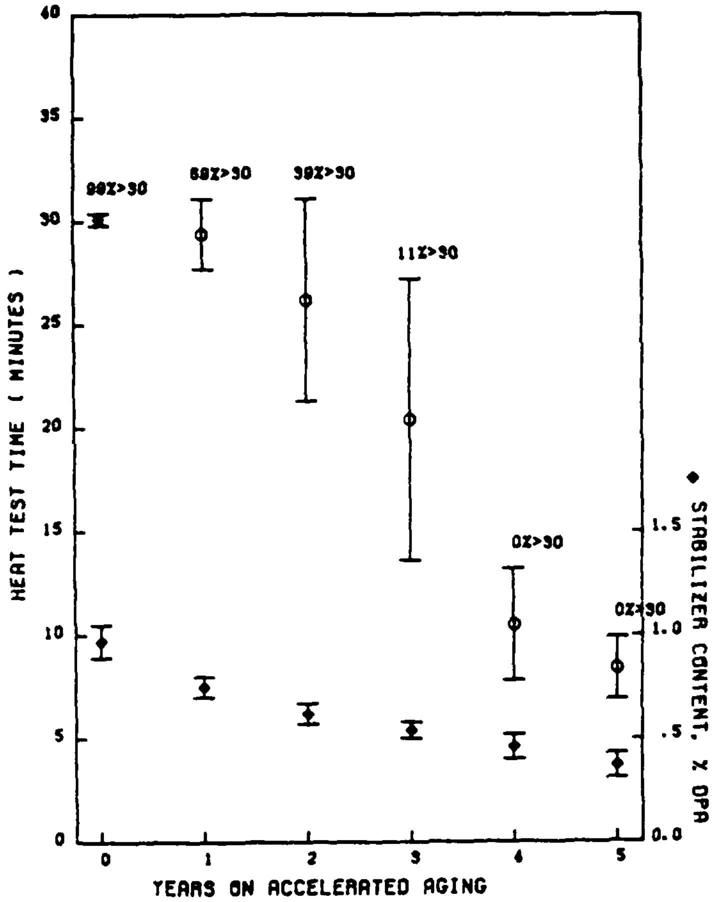

FIGURE 21 Mean stabilizer content and mean heat test time on ageing (5 years), NH025 [NC 86, DNT 10, DBP 3, DPA 1] (1945-1957), heat test temperature 71°C.

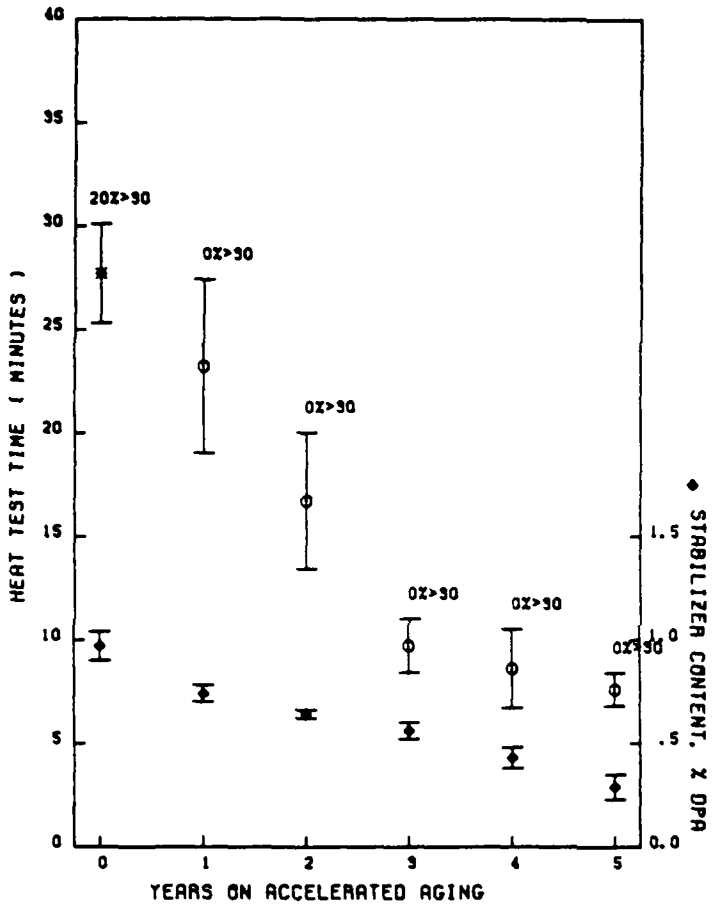

FIGURE 22 Mean stabilizer content and mean heat test time on ageing (5 years), FNH/P [NC 83, DNT 10, DBP 5, DPA 1, K1] (1957-1979), heat test temperature 82°C initial, then 71°C.

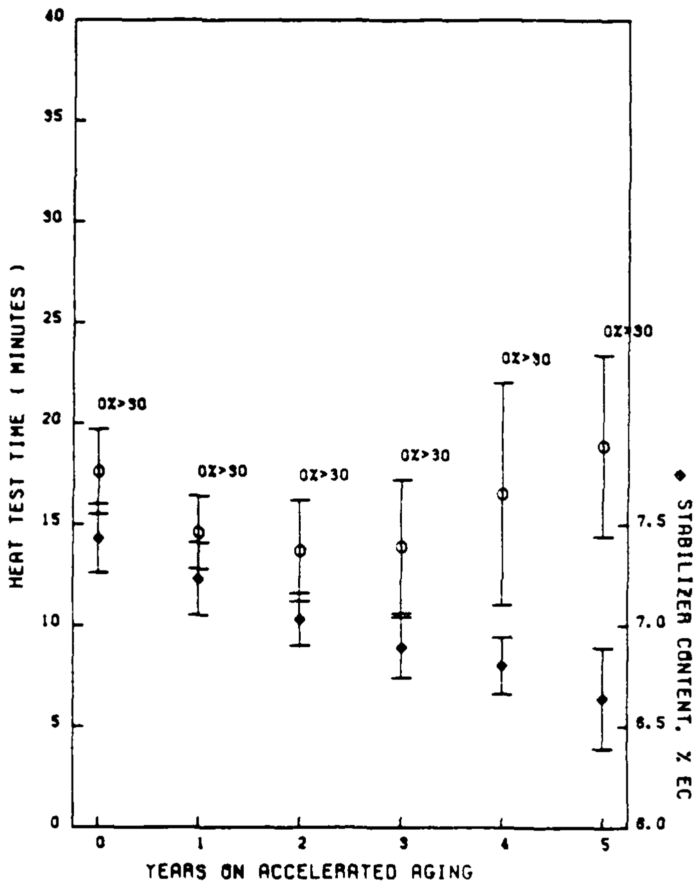

FIGURE 23 Mean stabilizer content and mean heat test time on ageing (5 years), NFQ042 [NC 16.45, NG 20.95, NQ 54.8, EC 7.5, CR] (1944-1953), heat test temperature 65.6°C.

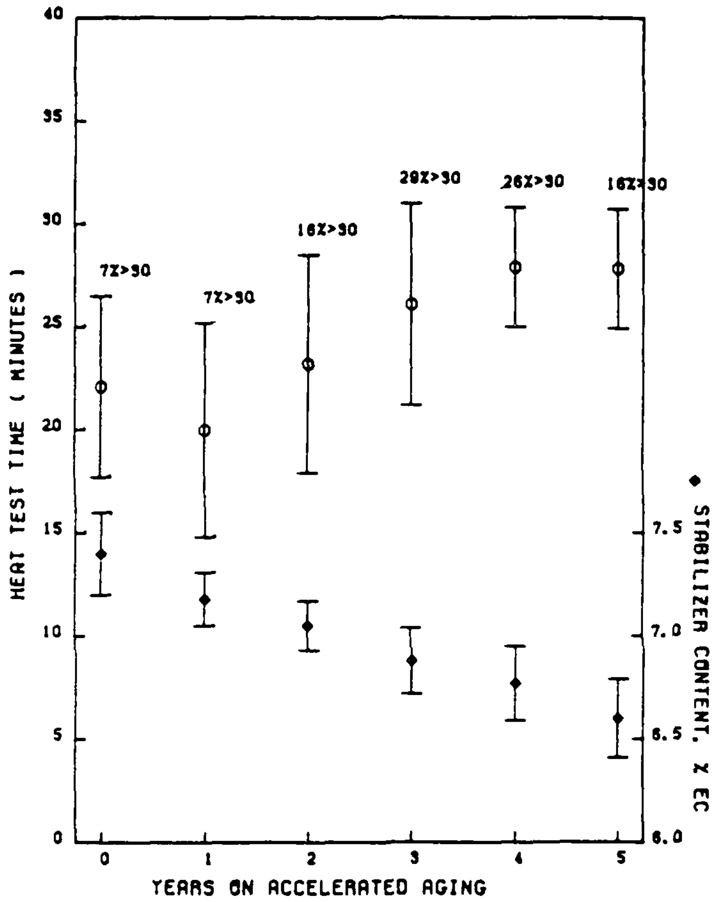

FIGURE 24 Mean stabilizer content and mean heat test time on ageing (5 years), MNF/S [NC 16.45, NG 20.95, NQ 54.8, EC 7.5, CR] (1950-1968), heat test temperature 65.6°C.

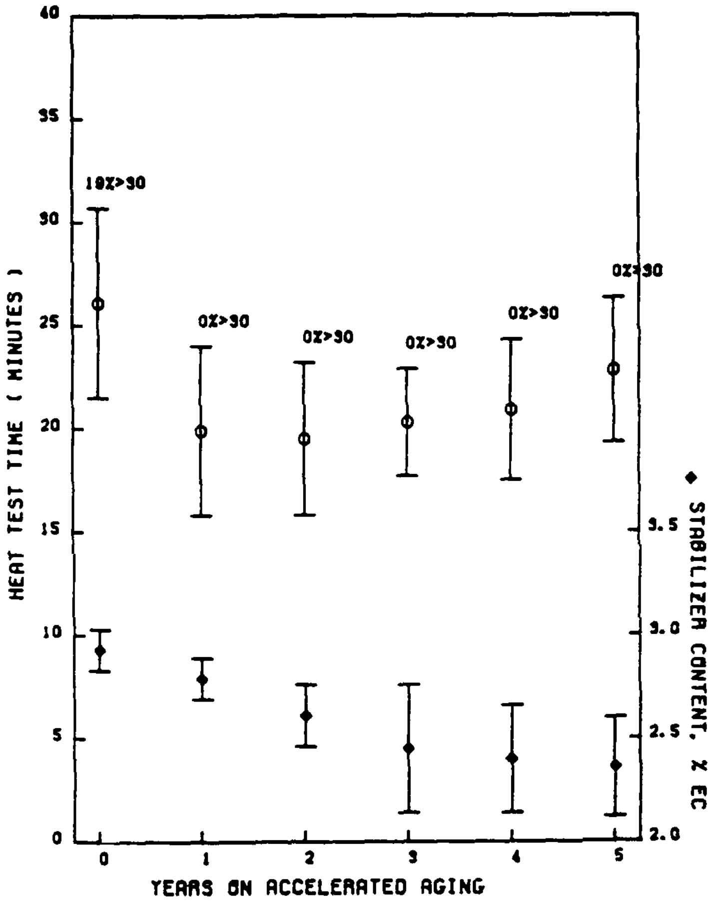

FIGURE 25 Mean stabilizer content and mean heat test time on ageing (5 years), MNQF/S032 (NC 20.95, NG 20.95, NQ 54.8, EC 3, CR) (1969-1977), heat test temperature 65.6^{o}C.